MASS TRANSPORT IN BIOREACTORS FOR COAL SYNTHESIS GAS FERMENTATION

K. T. Klasson, M. D. Ackerson, E. C. Clausen, and J. L. Gaddy
Department of Chemical Engineering
University of Arkansas
Fayetteville, AR 72701

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INTRODUCTION

Synthesis gas, a mixture of primarily CO, H_2 and CO_2, is a major building block in the production of fuels and chemicals. The gas is derived from non-gaseous raw materials such as coal, shale oil, tar sands, heavy residue and biomass. The composition of synthesis gas is dependent upon the raw materials used and the gasification process. Coal-derived gas is rich in CO and H_2, with lower concentrations of CO_2 and CH_4 and traces of H_2S and COS (1).

A wide variety of both liquid and gaseous fuels may be produced from synthesis gas using Fischer-Tropsch synthesis including light hydrocarbons (methane, ethane), fuel range hydrocarbon distillates and heavy waxes. The stoichiometry for product formation may be characterized by the empirical relation (2):

$$CO + 2.12\ H_2 \rightarrow (HC, Alcohols, Acids) + 0.95\ H_2O \quad (1)$$

As is noted, about 2 moles of H_2 are required for every mole of CO.

Since typical synthesis gas is deficient i H_2, a catalytic water gas shift conversion is used to adjust the H_2/CO ratio:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

This same reaction may be carried out biologically at ambient conditions with high yield using bacteria such as *Rhodospirillum rubrum* (3) or *Rhodopseudomonas gelatinosa* (4).

Purpose

The purpose of this paper is to present laboratory data from continuous culture experiments for the conversion of H_2O and CO in synthesis gas to CO_2 and H_2 using a biological process. The photosynthetic bacterium *R. rubrum* is employed. Performance results from continuous stirred tank and trickle-bed reactors are presented and discussed.

BIOREACTOR DESIGN

The choice of a suitable bioreactor for synthesis gas fermentations is a matter of matching reaction kinetics with the capabilities of the various reactors. It has been found that for these slightly soluble gases, the rate

of mass transfer usually controls the reactor size (5,6). Mass transfer capabilities of the reactor must be balanced with the cell density achieved. The proper reactors for these systems will likely be ones that achieve high mass transfer rates and high cell densities. These concepts will be expanded in this and the following section.

Gas-Liquid Mass Transfer Concepts

The transfer of gas phase substrates in fermentation systems involves three heterogeneous phases: the bulk gas phase, the culture medium (liquid) and microbial cells (solid) suspended in the medium. The reactants, present in the gas phase, must be transported across the gas-liquid interface and diffuse through the culture medium to the cell surface to be consumed by the microbes. In general, a combination of the following resistances can be expected (7):

1. Diffusion through the bulk gas to the gas-liquid interface.
2. Movement across the gas-liquid interface.
3. Diffusion of the solute through the relatively unmixed liquid region (film) adjacent to the bubble and into the well-mixed bulk liquid.
4. Transport of the solute through the bulk liquid to the stagnant film surrounding the microbial species.
5. Transport through the second unmixed liquid film associated with the microbes.
6. Diffusive transport across the liquid/solid boundary and into the microbial floc, mycelia, or particle, if appropriate. When the microbes take the form of individual cells, this resistance disappears.
7. Transport across the cell envelope to the intracellular reaction site.

As with the conventional chemical engineering analysis of absorption processes, mass transfer through the bulk gas phase is assumed to be instantaneous. Also, when individual cells are suspended in a medium, the liquid film resistance around the cells is usually neglected with respect to other resistances, because of the minute size and the enormous total surface of the cells (8). Thus, for the transfer of sparingly soluble gases, such as CO, the primary resistance to transport may be assumed to be in the liquid film at the gas-liquid interface.

It can be shown that the substrate transfer rate per unit of reactor volume, $\frac{dN_S^G}{V_L dt}$, is given in terms of the gas phase partial pressures as:

$$\frac{d\,N_S^G}{V_L dt} = \frac{K_L a}{H}\,(P_S^G - P_S^L) \qquad (3)$$

where N_S^G = moles substrate transferred from the gas phase, V_L is the volume of the liquid phase, t is time, K_L is the overall mass transfer coefficient,

a is the gas-liquid interfacial area per unit volume, H is Henry's law constant, P_S^G is the partial pressure of the substrate in the bulk gas phase, and P_S^L is the partial paressure (dissolved tension) of the substrate in the liquid phase ($P_S^G = HC_L$). The rate of transport from the gas phase must be equal to the rate of consumption in the liquid phase, given by a Monod relationship:

$$\frac{d N_S^G}{V_L dt} = \frac{X q_m P_S^L}{K'_p + P_S^L + (P_S^L)^2/W'} = \frac{K_L a}{H} \left[P_S^G - P_S^L\right] \qquad (4)$$

where X is the cell concentration and q_m, K'_p, and W' are Monod constants.

Equation (4) shows that a bioreactor for these gaseous systems must operate in either of two regimes. In one case, sufficient cells are present to react more solute, but the mass-transfer rate cannot keep pace. Therefore, the liquid phase concentration goes to zero and the reactor is mass transport limited. The cell concentration and rate of consumption are limited by the ability of that particular reactor to transfer substrate. In the other case, sufficient substrate can be supplied, but the cell concentration does not allow consumption at an equal rate. Then the liquid phase concentration is not zero (with possible inhibitory effects) and the rate is limited by the cell concentrations in that particular bioreactor. Obviously, the best bioreactor is one that will achieve high cell concentrations and high mass transfer rates.

Stirred Tank Reactor Studies

The traditional reactor used in continuous fermentation processes is the stirred tank reactor, or CSTR. As it relates to gas phase substrates, the CSTR has continuous gas flow into a constant volume liquid phase reactor. A small liquid feed stream is utilized to supply nutrients to the microorganisms in the reactor system and to remove products. The agitation rate in the system is relatively high in order to promote transfer of the sparingly soluble gas into the liquid culture medium.

Experiments have been carried out in a CSTR at different gas flow rates under mass transfer-limited conditions. In these experiments, the progress of the reaction is followed by the use of an inert component, whose partial pressure does not change throughout the system. Assuming perfect mixing in both the gas and the liquid phases, the CO uptake rate from the gas phase may be described by Equation (5) under mass transfer limiting conditions:

$$\dot{n}_I (Y_{CO}^i - Y_{CO}^o) = \frac{K_L a}{H} \cdot V_L \cdot P_{CO}^o \qquad (5)$$

Equation (5) may be easily rearranged to yield:

$$\left(\frac{P_{CO}^i}{P_{CO}^o} - \frac{P_I^i}{P_I^o} \right) = \frac{K_L a}{H} \cdot \frac{V_L \cdot RT}{G^i} \qquad (6)$$

A plot of CO conversion as a function of pseudo retention time in the CSTR (defined as the liquid volume in the reactor divided by the gas flow rate) is shown in Figure 1. As noted, a conversion of about 55 percent was attained at a retention time of 1 h. The maximum conversion was about 85 percent, attained at retention times of 3 h or above. Conversion in the CSTR is limited by the mixed flow pattern inside the reactor.

The mass transfer coefficient, K_La, may be obtained for the CSTR experiments by employing Equation (6). If the left hand side of Equation (6) is plotted as a function of V_L RT/HG a straight line should be obtained with a slope of K_La if the experiments are carried out under mass transfer limiting conditions. Such a plot is shown in Figure 2, where K_La is shown to have a value of 70.0 h^{-1}. It should be noted that these experiments were carried out at a constant agitation rate of 400 rpm. Agitation rate, impeller design and other physical characteristics of the reactor significantly affect the value of the mass transfer coefficient.

Trickle Bed Reactor Studies

Trickle-bed reactors are used conventially to obtain a low pressure drop or low liquid holdup when there is practically no heat to remove or supply, or the liquid is corrosive. They are usually operated countercurrently since a higher driving force can be achieved than with cocurrent operation. However, when an irreversible reaction occurs between the dissolved gases and the absorbent (as in biological systems), the mean concentration driving force is the same for both modes of operation. In this case, the capacity of cocurrent columns is not limited by flooding and at any given flow rates of gas and liquid, the pressure drop in a cocurrent column is less (9).

Experiments were conducted in a cocurrent column packed with ceramic Intalox saddles. In this experimental setup, the liquid and the gas were disengaged in a liquid/gas separator with the culture being recirculated back to the top of the column. In this manner, a high concentration of cells can be maintained inside the reactor while at the same time using high L/G operating conditions inside the column. For this ystem, assuming perfect plug flow in the gas phase ascending through the column and constant partial pressure of the inert gas in the system (as closely substantiated from experimental data), the outlet ratio of CO to the inert can be related to other operating conditions according to the equation (10):

$$\ln \frac{Y^i_{CO}}{Y^o_{CO}} = K_L a' \frac{ShRT}{H\,\bar{G}} \qquad (7)$$

A plot of CO conversion as a function of pseudo retention time in the trickle bed reactor is shown in Figure 3. In contrast to the CSTR results, nearly complete conversion was seen in the trickle bed at a retention time of 0.6 h. Complete conversion was obtained because the trickle bed operates very closely to ideal plug flow behavior.

Figure 4 shows the calculation of the mass transfer coefficient for the trickle bed as a rearrangement of Equation (7). The value of K_La of 23.5 h^{-1} is in good agreement with the value of 27.0 h^{-1} calculated from the results of Charpentier (9).

CONCLUSIONS

The performance of *R. rubrum* in producing H_2 was demonstrated in a continuous stirred tank reactor and a trickle-bed reactor. A conversion of 0.85 was obtained in the CSTR at a pseudo retention time of 3 h. The plug flow trickle-bed reactor gave a conversion of 100 percent at a retention time of only 0.6 h. Mass transfer coefficients were obtained for the two continuous reactors, with K_La equaling 70.0 h^{-1} in the CSTR and 23.5 h^{-1} in the trickle-bed reactor.

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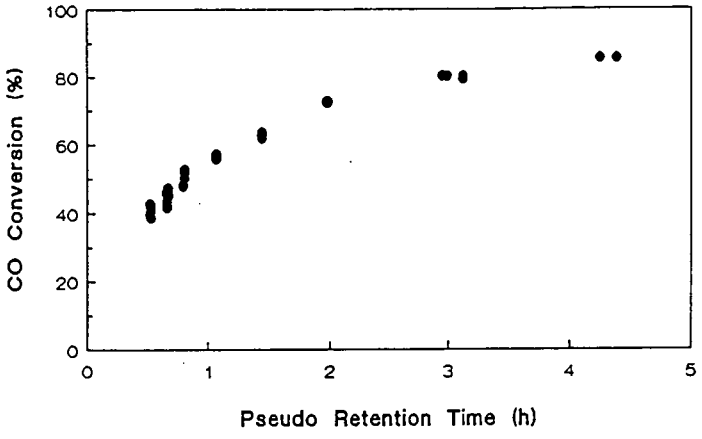

Figure 1. CO conversion profile in the CSTR at various pseudo retention times

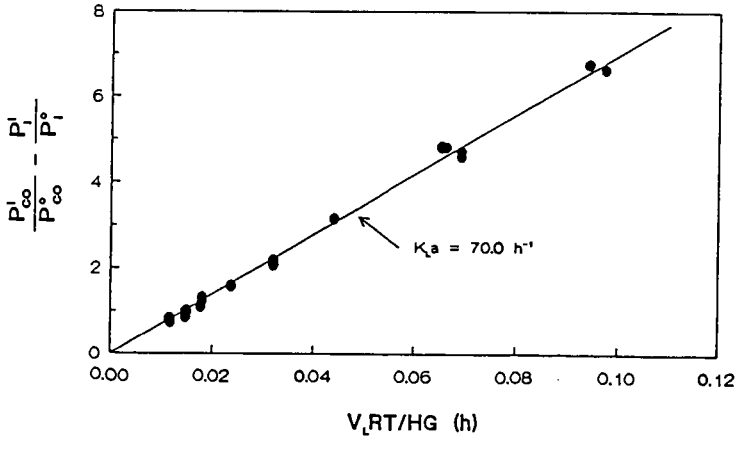

Figure 2. Determination of the mass transfer coefficient in the CSTR

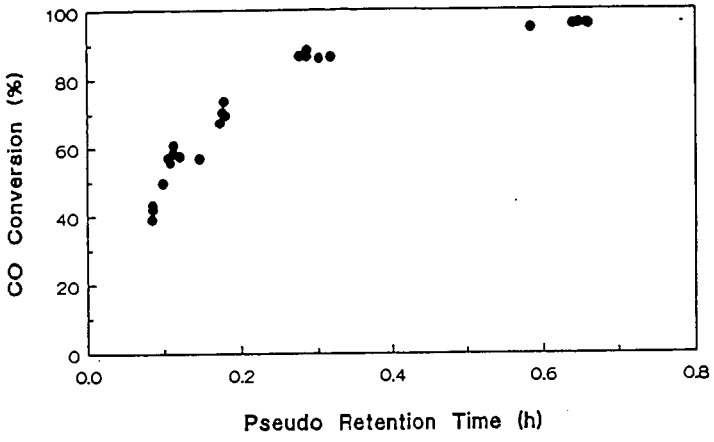

Figure 3. CO conversion profile in the trickle-bed reactor at various pseudo retention times.

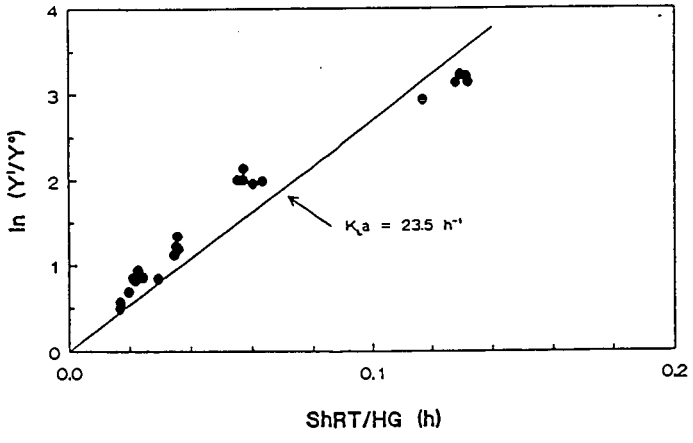

Figure 4. Determination of the mass transfer coefficient in the trickle-bed reactor